Chapter 6

Structure of the Atom

Current model of the atom:

Protons and neutrons comprise the nucleus;

Electrons are located outside the nucleus.

Ernest Rutherford receives primary credit for this model of the atom.

Goal for this chapter is to understand the behavior of the electron in an atom, its energy is location and what happens to it in chemical reactions.

Structure of the Atom

What is our model of the behavior of the electron?

Historically, is was that the electron orbited the nucleus.

Modern, the electron occupies an orbital. An orbital is a 3-dimensional region of space where the probability of finding the electron is high.

Structure of the Atom

What happens when an aqueous solution of metal ions are heated.

Structure of the Atom

What happens when an aqueous solution of metal ions are heated.

Spectra

We see cool colors…where are those colors coming from? What causes those colors? Why are they different?

To understand we need to first consider some properties of waves…of light.

We are familiar with light. The light our eyes are sensitive to occupies a small region of the electromagnetic spectrum.

Structure of the Atom

Light is best model as oscillating magnetic and electric fields.

The electromagnetic spectrum consists of light waves of different wavelengths.

Structure of the Atom

For electromagnetic radiation

Wavelength –λ– lambda (10^{-9} m = 1 nm)

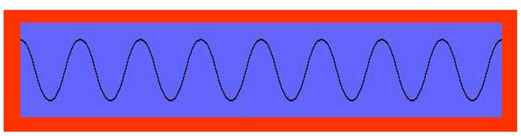
Frequency –ν– nu (cycles per second, s^{-1} or Hz)

The speed of light is a constant - 3.00 x 10^{8} m/s

$c = \lambda/\nu$

Structure of the Atom

The distance from the left side of the box to the right side of the box is 2.4 meters, calculate the wavelength of the wave.



Structure of the Atom

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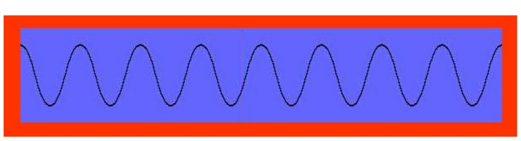
2.4 meters/8 wavelengths = 0.3 meters = λ

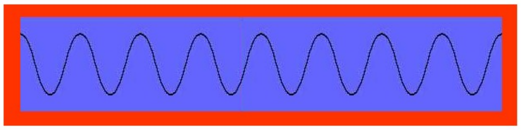


Structure of the Atom

The distance from the left side of the box to the right side of the box is 2.4 meters, calculate the wavelength of the wave.

λ = 0.3 meters

$\nu = c/\lambda = 3.00 \times 10^8\ m \cdot s^{-1}/0.3\ m = 1 \times 10^9\ s^{-1}$



Structure of the Atom

Calculate the frequency of light that has a wavelength of 6.7×10^{-5} cm.

$\lambda = 6.7 \times 10^{-5}$ cm

6.7×10^{-5} cm (1 m/100 cm) = 6.7×10^{-7} m

$\nu = c/\lambda = 3.00 \times 10^8\ m \cdot s^{-1}/ 6.7 \times 10^{-7}\ m = 4.8 \times 10^{14}\ s^{-1}$

Photon: A quantum of light

The smallest unit of matter is an atom.

Matter can be subdivided into basic units called atom. We can not have fractions of atoms.

An atom is a quantum of matter.

Photon: A quantum of light

In 1900, investigations of relationship between the frequency and the energy of light emitted by hot, solid objects could not be explained using classical physics.

Max Planck found he could explain the relationship between energy and frequency by introducing a constant, AND by hypothesizing that the light emitted by hot, solids could only have discrete amounts.

$$E = h\nu$$

Photon: A quantum of light

According to Planck's relationship, light that was emitted by hot, solids could only have energies,

$$E = h\nu, \text{ or } 2h\nu, \text{ or } 3h\nu\ldots.$$

Classical mechanics said the energy could have any values, Planck's model indicated that the only way to explain the experiments was to assume that the energy released or absorbed could only have discrete values of $h\nu$.

Photon: A quantum of light

The smallest amount of energy is given as

$$E = h\nu, \text{ or } 2h\nu, \text{ or } 3h\nu\ldots.$$

where h is a constant called Planck's constant and has a value,

$h = 6.626 \times 10^{-34}$ J·s

$E = h\nu$ or $E = hc/\lambda$

Photon: A quantum of light

In 1905 Albert Einstein used Planck's model of quantized light to explain the Photoelectric effect.

When light shines on a metal surface, a beam of electrons is produced. Einstein explained this experimental observation by assuming that light is composed of packets called photons.

Einstein explained the Photoelectric effect as photons of light strike atoms on the surface and transfer their energy to certain electrons in the surface atoms…ejecting the electrons.

Photon: A quantum of light

Einstein explained the Photoelectric effect as photons of light strike atoms on the surface and transfer their energy to certain electrons in the surface atoms…ejecting the electrons.

Thinking of light as composed of packets, or particles, (photons) of energy, suggests that light, which we had started talking about as a wave, might also behaved as a particle.

Photon: A quantum of light

How might we use the relationship between energy and frequency for light?

$E = h\nu$

Calculate the energy of photons of orange light with a frequency of 5.0×10^{14} s^{-1}.

Photon: A quantum of light

Calculate the energy of photons of orange light with a frequency of

$5.0 \times 10^{14}\ s^{-1}$ · h (planck's constant has a value of $6.626 \times 10^{-34}\ J\ s^{-1}\ photon^{-1}$

$E = h\nu = 6.626 \times 10^{-34}\ J\ s\ photon^{-1} \cdot 5.0 \times 10^{14}\ s^{-1}$

$E = h\nu = 3.31 \times 10^{-19}\ J\ photon^{-1}$

The energy of a photon of orange light is 3.31×10^{-19} J

Photon: A quantum of light

What is the energy of a mol of photons of orange light with a frequency of $5.0 \times 10^{14}\ s^{-1}$

$3.31 \times 10^{-19}\ J\ photon^{-1} \cdot 6.02 \times 10^{23}\ photon/1\ mol$
$= 1.99 \times 10^{6}$ J or 199 kJ

The energy of a mol of photon of orange light is 199 kJ

Photon: A quantum of light

The energy required to break the oxygen-oxygen bond in O_2 is 496 kJ mol^{-1}. Calculate the minimum wavelength of light that can break the oxygen-oxygen bond.

Photon: A quantum of light

The energy required to break the oxygen-oxygen bond in O_2 is 496 kJ mol^{-1}. Calculate the minimum wavelength of light that can break the oxygen-oxygen bond.

First we need to convert the bond energy from kJ mol^{-1} to J $molecule^{-1}$

$$496 \text{ kJ/mol} \cdot (1000 \text{ J/1 kJ}) \cdot (1 \text{ mol}/6.02 \times 10^{23} \text{ molecules})$$
$$= 8.24 \times 10^{-19} \text{ J molecule}^{-1}$$

Now we can calculate the wavelength of a photon with this amount of energy.

$$E = h\nu = hc/\lambda$$
$$\lambda = hc/E$$
$$\lambda = (6.626 \times 10^{-34} \text{ J s photon}^{-1} \cdot 3.00 \times 10^{8} \text{ m s}^{-1})/8.24 \times 10^{-19} \text{ J molecule}^{-1}$$
$$\lambda = 2.41 \times 10^{-7} \text{ m} = 241 \text{ nm}$$

Photon: A quantum of light

Light is quantized, and is made up of discrete packets called photons.

Matter is quantized, and is made up of discrete packets called atoms.

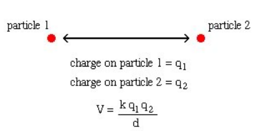
Shell Model

Look at the trend in ionization energies for the first 20 elements.

Discuss the shell model of the atom.

Electrons are attracted more strongly as nuclear charge increases

Electrons are attracted less strongly as the distance from the nucleus increases.



Shell Model

Ionization

$$H(g) \rightarrow H^{+}(g) + 1e^{-}$$

The energy to do this is 1312 kJ mol^{-1}

(Note: the energy is endothermic and this is the same energy we calculat using the Bohr model. $\Delta E = -2.18 \times 10^{-18}$ J $(1/n_f^2 - 1/n_i^2)$)

For helium

$$He(g) \rightarrow He^{+}(g) + 1e^{-}$$

The energy to do this is 2372 kJ mol^{-1}

Must conclude that if it take about twice the energy to remove an electron in helium that the electron must be about the same distance fron the nucleus as the electron in hydrogen.

Shell Model

Ionization

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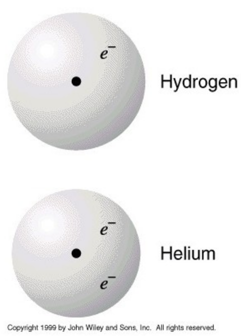

Shell Model

Ionization

$$Li(g) \rightarrow Li^{+}(g) + 1e^{-}$$

The energy to do this is 520 kJ mol^{-1}

Hmmm…a drop in ionization energy…even though the nuclear charge i now three times the nuclear charge on hydrogen…the IE is SMALLER!

We can only conclude that this electron can not be the same distance from the nucleus as the electrons in hydrogen and helium, it must be further from the nucleus.

$$Be(g) \rightarrow Be^{+}(g) + 1e^{-}$$

The energy to do this is 899 kJ mol^{-1}

Now this IE is higher. This electron can not be the same distance as the electrons in H and He, but it must be about the same distance as the electron in Li.

Shell Model

Ionization

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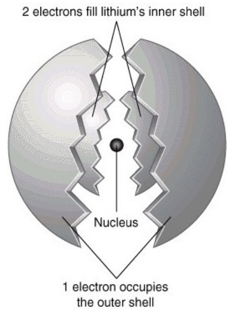
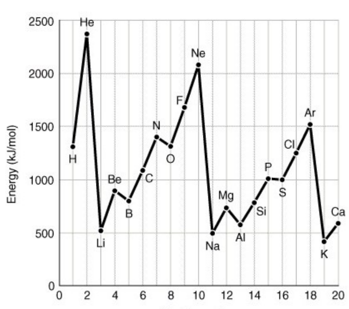


Shell Model

Symbol	Z	IE (kJ mol^{-1})	Symbol	Z	IE (kJ mol^{-1})
H	1	1312	Na	11	496
He	2	2370	Mg	12	738
Li	3	520	Al	13	578
Be	4	900	Si	14	786
B	5	800	P	15	1012
C	6	1090	S	16	1000
N	7	1400	Cl	17	1250
O	8	1314	Ar	18	1520
F	9	1680	K	19	418
Ne	10	2080	Ca	20	590

Shell Model



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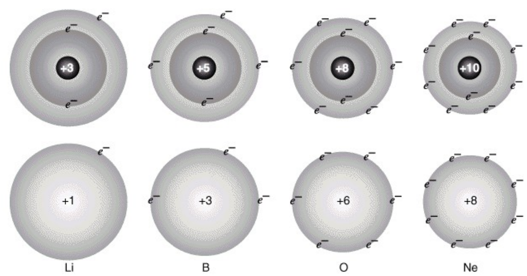
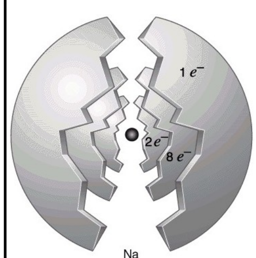
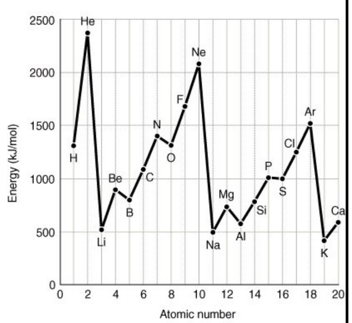
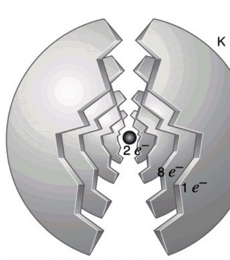


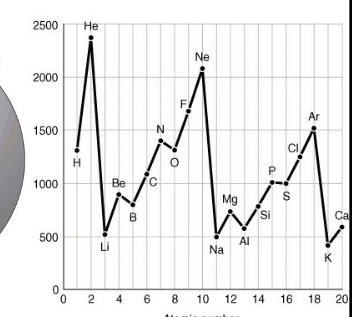
Shell Model





Shell Model





Shell Model

From the first ionization energies we see that the electrons in elements occupy shells. Each shell is further from the nucleus.

However, the ionization energy reflects the energy required to remove the electron furthest from the nucleus…the easiest electron to remove.

What about the other electrons in each element?

For those elements with many electrons what happens to the energy of the other electrons in the inner shells? Do all electrons within each shell have the same energy?

Shell Model

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Using Photoelectron spectroscopy (PES) the energy of any electron in an atom can be measured.

Shell Model

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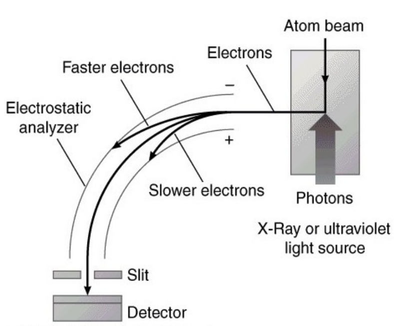
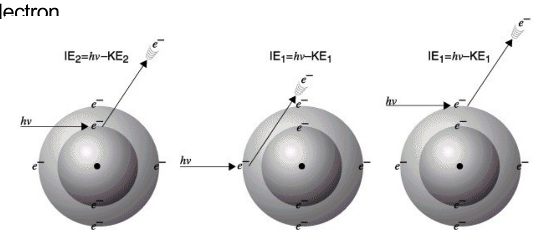


In the experiment a beam of atoms absorbs a high energy photon (UV or X-ray). The energy of the photons exceed the ionization energy, so any electron can be removed. When the electron is removed it will require some energy, the excess energy absorbed by the electron takes the form of kinetic energy.

Shell Model

In the experiment a beam of atoms absorbs a high energy photon (UV or X-ray). The energy of the photons exceed the ionization energy, so any electron can be removed. When the electron is removed it will require some energy, the excess energy absorbed by the electron takes the form of kinetic energy. We know hν, and we know KE, so we can calculate the ionization energy for every electron



Shell Model

So what does a PES spectrum look like?

Shell Model

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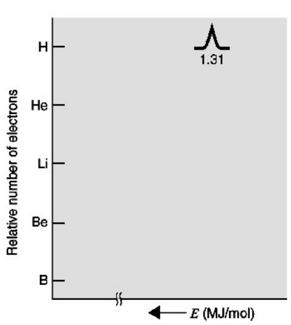


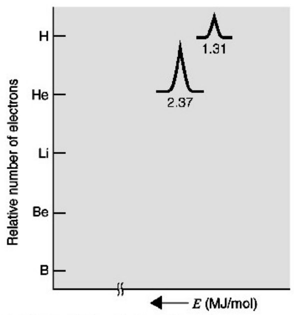
The spectrum consists of a plot of energy (x-axis) versus the relative number of electrons.

This spectrum shows the hydrogen atom. Note that the energy on the x-axis increases going to the left.

The height of the peak is a measure of the number of electrons at that energy.

Shell Model

So what does a PES spectrum look like?

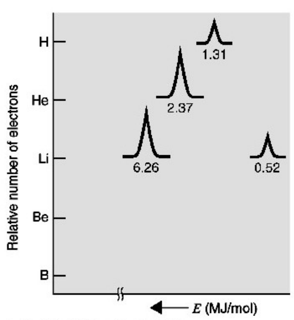


This spectrum shows the helium and hydrogen atom. Note that the energy on the x-axis increases going to the left.

For helium notice the peak height is double the peak height for hydrogen, so both electrons have the same energy. Also the energy of the electrons is greater. The greater nuclear charge on the helium nucleus, the electrons must be the same distance as the electron in hydrogen.

Shell Model

So what does a PES spectrum look like?

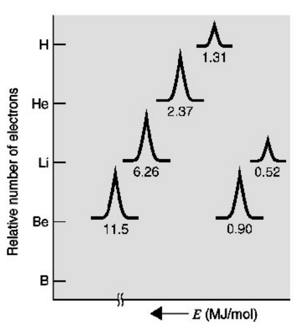


This spectrum adds the lithium atom. Note that the energy on the x-axis increases going to the left.

The three electrons have different energies. Two electrons require more energy (6.26 MJ) to remove, these are the electrons in the first shell. The electron at lower energy (0.52 MJ) is in a different shell, further from the nucleus, and easier to remove.

Shell Model

So what does a PES spectrum look like?



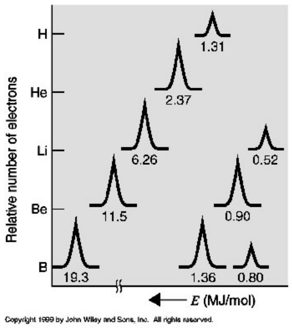
This spectrum adds the beryllium atom. Note that the energy on the x-axis increases going to the left.

The four electrons are distributed with two in the first shell and two in the second shell. The two electron in the second shell have the same energy (0.90 MJ).

I wonder what the spectrum for boron will look like?

Shell Model

So what does a PES spectrum look like?



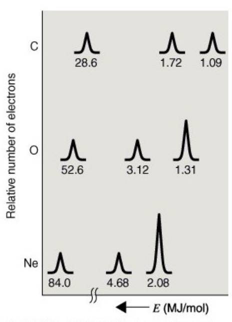
This spectrum adds the boron atom. Note that the energy on the x-axis increases going to the left.

OK, now this is different! There are two electrons in first shell, as always, but there is a new peak with one electron that is a little easier to remove compared to the electrons in the second peak.

What happens with carbon, nitrogen…and the remaining elements in the second period?

Shell Model

So what does a PES spectrum look like?



This spectrum shows carbon, oxygen and neon.

Notice the first two peaks maintain the same number of electrons, but the third peak increases in intensity. For carbon there are two electrons in the third peak, four electrons for oxygen and six electrons for neon.

Moving across the period the energy required to remove an electron continues to increase, so the electrons in the second and third peak are in the same second shell. However, the second shell has two different types of electrons. To account for this the idea of a subshell can be used.

Shell Model

So the model of the atom with many electrons uses the idea of shells and subshells.

We have described the shells in terms of first, second, third, etc. So shells have values of 1, 2, 3, 4 …. We use the variable n to denote the value of a shell.

Hydrogen has one electron in the n = 1 shell, while carbon (6 electrons) has 2 in the n = 1 shell and four electrons in the n = 2 shell.

Subshells were assigned letters; *s, p, d and f*. So every electron in an atom has an assigned shell value and an assigned subshell value.

The second shell has two subshells, so we assume the first shell has only one subshell. PES data supports the existence of three subshells in the third shell, and four subshells in the fourth shell.

Shell Model

Discuss Photoelectron Spectroscopy

Electrons in levels have different energies.

n = 1 : 1 sublevel; called the 's' sublevel

the 1s sublevel can hold 2 electrons;

n = 2 : 2 sublevels; first called the 's' sublevel; second called the 'p' sublevel

the 2s sublevel can hold 2 electrons;

the 2p sublevel can hold 6 electrons;

n = 3 : 3 sublevels; first called the 's' sublevel; second called the 'p' sublevel; third called the 'd' sublevel

the 3s sublevel can hold 2 electrons;

the 3p sublevel can hold 6 electrons;

the 3d sublevel can hold 10 electrons;

Shell Model

For an element we can describe the location of each of its electrons in terms of the shell and subshell.

H – $1s^1$;	Na – $1s^22s^22p^63s^1$;
He – $1s^2$;	Mg – $1s^22s^22p^63s^2$;
Li – $1s^22s^1$;	Al – $1s^22s^22p^63s^23p^1$;
Be – $1s^22s^2$;	Si – $1s^22s^22p^63s^23p^2$;
B – $1s^22s^22p^1$;	P – $1s^22s^22p^63s^23p^3$;
C – $1s^22s^22p^2$;	S – $1s^22s^22p^63s^23p^4$;
N – $1s^22s^22p^3$;	Cl – $1s^22s^22p^63s^23p^5$;
O – $1s^22s^22p^4$;	Ar – $1s^22s^22p^63s^23p^6$;
F – $1s^22s^22p^5$;	K – $1s^22s^22p^63s^23p^64s^1$;
Ne – $1s^22s^22p^6$;	Ca – $1s^22s^22p^63s^23p^64s^2$;

Shell Model

For an element we can describe the location of each of its electrons in terms of the shell and subshell.

Sc – $1s^22s^22p^63s^23p^64s^23d^1$;	
Ti – $1s^22s^22p^63s^23p^64s^23d^2$;	
V – $1s^22s^22p^63s^23p^64s^23d^3$;	
.	
.	
.	
.	
Zn – $1s^22s^22p^63s^23p^64s^23d^{10}$;	
Ga – $1s^22s^22p^63s^23p^64s^23d^{10}4p^1$;	

Orbitals

For electrons we know two properties: its mass and its charge.

As a result of further experimentation (Stern-Gerlach) another important property of electrons was characterized….

When silver atoms are heated from a surface and passed through a slit, through a magnetic field where the path of the silver atoms are bent.

The silver atoms then collide with a glass window…and two silver mirrors are produced next to each other. The silver atoms interact with the magnetic field in two distinct ways.

Orbitals

These results were interpreted by assuming the electron had a third physical property which was called spin.

When an electron is spinning it will produce its own magnetic field. The previous experiment suggested that electrons produced their own magnetic field.

So our model of the electron now includes spin; two spins labeled

+1/2 and –1/2

Two electrons with opposite spin are described as paired.

An element with an unpaired electron will exhibit magnetic properties.

Orbitals

Also according to our model of the atom that electrons with the same spin do NOT like to occupy the same region of space. However, when electrons have opposite spins they can occupy the same region of space.

This region of space is called an orbital.

Orbitals are 3-dimensional regions of space (of different shapes as we will soon see) that can hold a maximum of 2 electrons. The Pauli Exclusion Principle says that no more than two electrons can be found in any orbital, and their spins must be opposite.

Since electrons are negatively charged, even when they are in the same orbital they repel each other.

Orbitals

When we review the subshells found in shells we note that there are always even numbers of electrons in the subshells.

So subshells will consist of different numbers of orbitals;

The first shell has one s subshell that has only 1 orbital, called the 1s orbital which holds two electrons;

The second shell has two subshells: 2s subshell with one orbital and the 2p subshell with three orbitals. The 2p subshell can hold 6 electrons, so there must be three 2p orbitals in a 2p subshell.

In the third shell there are three subshells: 3s, 3p and the 3d. The 3d subshell has 10 electrons….five orbitals. There are five 3d orbitals in the 3d subshell.

Electron Configurations

We now look at the electron configurations for the elements in the perio table in terms of shells, subshells and orbitals.

Animation

Shapes of Orbitals

We now look at the electron configurations for the elements in the perio table in terms of shells, subshells and orbitals.

Periodic Table with orbital shapes

Dual Nature of Matter and Light

It had been demonstrated that depending on the experiment electromagnetic radiation could behave as a wave (diffraction of light) or as a particle (Photoelectricc Effect). Compton also demonstrated that photons could behave as particles in a different type o experiment.

Louis de Broglie postulated that matter could demonstrate both particle and wave-like properties. A few years later researchers demonstrated that electrons could be diffracted…wavelike behavior. So electrons can behave as waves.

Results in the Heisenberg Uncertainty Principle it is impossible to know both the position and energy of a particle simultaneously. So for particles like electrons we can only speak of the probability of finding the electron in a region of space.

Bohr Model of the Hydrogen Atom

Light is quantized, and is made up of discrete packets called photons.

Matter is quantized, and is made up of discrete packets called atoms.

Experimental evidence and interpretation:

Emission spectrum of the hydrogen atom: visible region, ultraviolet region, infrared region, summary.

Bohr Model of the Hydrogen Atom

Experimental Evidence

Bohr model version I.

Bohr model version II

Bohr Model of the Hydrogen Atom

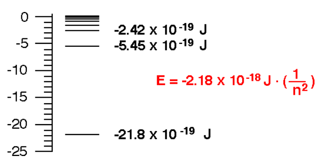
The Bohr model of the hydrogen atom establishes the possible energy levels the electron can have;

$E = -2.18 \times 10^{-18}\ J \cdot (1/n^2)$

where n can have values of 1, 2, 3, 4, etc

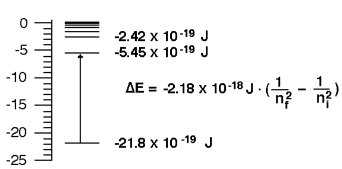
Bohr Model of the Hydrogen Atom

The Bohr model of the hydrogen atom



Bohr Model of the Hydrogen Atom

The Bohr model of the hydrogen atom



$\Delta E = -2.18 \times 10^{-18}\ J\ (1/2^2 - 1/1^2) = 1.64 \times 10^{-18}\ J$

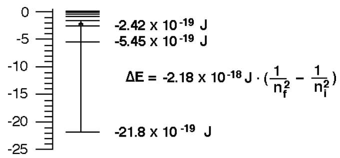
$\Delta E = h\nu$

$\nu = \Delta E/h = 1.64 \times 10^{-18}\ J / 6.626 \times 10^{-34}\ Js = 2.48 \times 10^{15}\ s^{-1}$

This is the first line in the Lyman Series.

Bohr Model of the Hydrogen Atom

Calculate the energy difference between the n = 1 and the n = 4 levels in a hydrogen atom. What is the energy of a photon that would excite an electron from the n = 1 level to the n = 4 level?



$\Delta E = -2.18 \times 10^{-18}$ J $(1/4^2 - 1/1^2) = 2.04 \times 10^{-18}$ J (energy of a photon that excites the electron from the n = 1 to n = 4 level.)

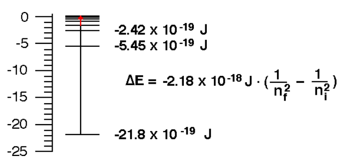
$\Delta E = h\nu$

$\nu = \Delta E/h = 2.04 \times 10^{-18}\ J / 6.626 \times 10^{-34}\ Js = 3.08 \times 10^{15}\ s^{-1}$

$\lambda = c / \nu = 3.00 \times 10^{8}\ ms^{-1} / 3.08 \times 10^{15}\ s^{-1} = 9.74 \times 10^{-8}\ m = 97.4\ nm$

Bohr Model of the Hydrogen Atom

Calculate the amount of energy required to ionize a hydrogen atom (remove the electron) when the electron is in the n = 1 level.



Bohr Model of the Hydrogen Atom

Which condition requires more energy to remove an electron:

when an electron is close to the nucleus, or when an electron is further from the nucleus? Explain.

When the nuclear charge is a +1 or when the nuclear charge is a +5 (assume the electron is the same distance from the nucleus)? Explain.